

Molecular Bridging in Asymmetric Triblock Copolymers

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Unlike immiscible homopolymers that generally phase-separate at macroscopic length scales, incompatible AB diblock copolymers are capable of spontaneous molecular self-organization into a variety of ordered morphologies at nanoscale dimensions. Classical block copolymer morphologies include A(B) spheres arranged on a cubic lattice in a B(A) matrix, A(B) cylinders arranged on a hexagonal lattice in a B(A) matrix and alternating lamellae. Equilibrium or metastable complex morphologies such as the gyroid or perforated lamellae, respectively, consist of bicontinuous channels exhibiting long-range order and spatial symmetry.

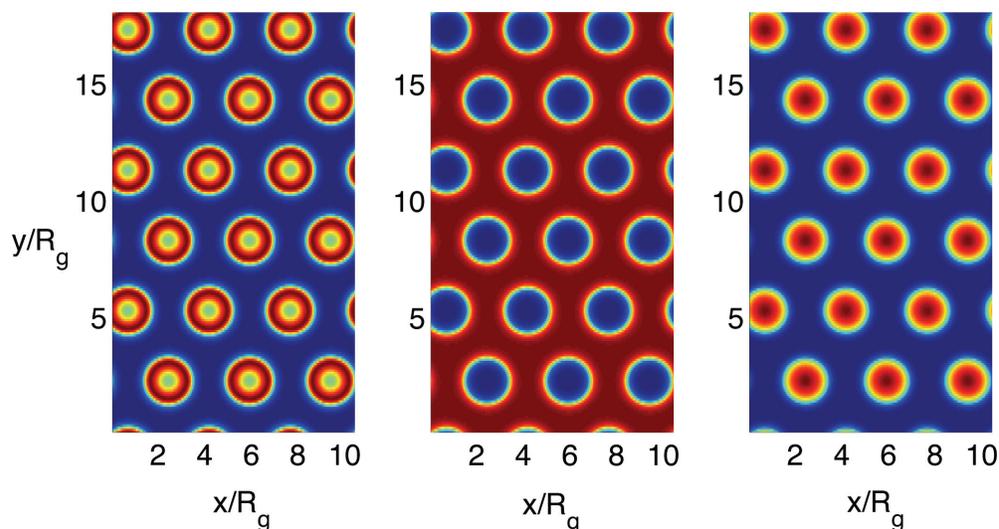
The ability to tune the morphologies of microphase-ordered block copolymers is critical to a broad range of emerging nanotechnologies and depends sensitively on the conformational entropy associated with interfacial chain packing. Molecular factors

governing interfacial chain packing include copolymer composition, repeat unit asymmetry and (liquid) crystallinity. The dependence of morphological development on interfacial chain packing is further amplified if a third block is added to a diblock copolymer, thereby forming a triblock copolymer. Incorporation of a dissimilar block results in the formation of an ABC triblock copolymer, which can greatly extend the assortment of experimentally accessible, and often hybrid, morphologies.

In this work, we focus on bicomponent ABA triblock copolymers wherein the third block is chemically identical to the first. Although these copolymers have been experimentally found and theoretically predicted to exhibit the same morphologies as their AB diblock counterparts, they can possess markedly different mechanical and flow properties due to the placement of the third block. If it resides in the same microdomain as the first, the B midblock forms a loop. If, on the other hand, the third block locates in a different microdomain, the midblock is forced to span two neighboring microdomains by forming a bridge. Experimental and theoretical studies have long sought to elucidate the conditions favoring, as well as the consequences of, molecular bridging in ABA triblock copolymer systems with limited success. These previous efforts have focused almost exclusively on molecularly (though not necessarily

Fig. 1.

Two-dimensional cross section of A rich cylindrical regions in a B rich matrix showing monomer density A_1 (left), B (center), and A_2 (right) for the case of a 16 kDa A_2 block. It is seen that the shorter A block (A_1 in this case) occupies the outer region of the A rich cylinders. Red color indicates high density and blue color indicates low density.



compositionally) symmetric copolymers wherein the endblocks are of identical length due to commercial interest in such materials as thermoplastic elastomers. Since midblock bridging clearly distinguishes an ordered ABA copolymer from its AB analog, a systematic study of the morphological and property development in molecularly asymmetric A_1BA_2 triblock copolymers progressively grown from a single A_1B diblock copolymer may be able to signal the onset of bridging.

The objective of this work is to discern the conditions signaling the origin of molecular bridging/looping in a series of isomorphous A_1BA_2 triblock copolymers from integrated experimental and self-consistent field theory analyses of morphological and property development as the A_2 block is chemically grown. A parent poly(styrene-*b*-isoprene) A_1B diblock copolymer, along with a series of molecularly asymmetric A_1BA_2 triblock copolymers, was synthesized. The block masses of the parent diblock were 9.4 kDa (styrene, A_1) and 46 kDa (isoprene, B), in which case the copolymer series is designated 9-46- A_2 , where the mass of the A_2 block was varied from 0kDa to 20kDa. This entire series was found, experimentally as well as theoretically, to form A-rich cylinders arranged on a hexagonal lattice. A two-dimensional cross section of this morphology is illustrated by Fig. 1. The spacing D of the cylinders were found to change nonmonotonically as the mass of the A_2 block is increased. As seen in Fig. 2 experiment and theory agree almost quantitatively on dependence of the spacing on the molecular weight of the A_2 block. The elastic

modulus of these materials has been experimentally determined to also depend nonmonotonously on the molecular weight of the A_2 block, with a dramatic increase as the A_2 block becomes large. The dramatic increase is believed to result from the chain's increased ability to bridge domains and form physical cross links between domains as the A_2 block is increased. We are currently working towards verifying this scenario by calculating the actual fraction of chains forming bridges between domains.

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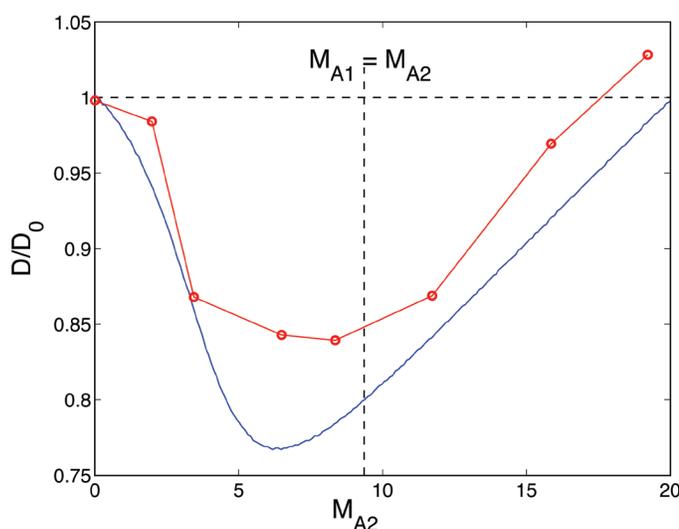


Fig. 2. Spacing D of cylinders normalized to the spacing D_0 of the diblock system vs molecular weight of the A_2 block. Experimental result is shown in red color and Self-Consistent Field Theory (SCFT) prediction is in blue.